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(21) International Application Number: PCT/KR99/00261 (22) International Filing Date: 26 May 1999 (26.05.99) (30) Priority Data: 1998/20010 30 May 1998 (30.05.98) KR (71)(72) Applicant and Inventor: KIM, Ho, Kyun [KR/KR]; Punglim Villa 102, 36-1, Nonhyeun-dong, Kangnam-ku, Seoul 135-010 (KR). (72) Inventor; and (75) Inventor/Applicant (for US only): WON, Seung, Ho [KR/KR]; Dongsan Apt. #1-603, Galma-dong, Seo-ku, Taejeon-city 302-171 (KR). (74) Agent: KIM, Nung, Kyun; Teakun Building, 6th floor, 822-5, Yoksam-dong, Kangnam-ku, Seoul 135-080 (KR).		(81) Designated States: AL, AM, AT, AU, BA, BB, BG, BR, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KR, KZ, LK, LR, LT, LU, LV, MD, MN, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TR, UA, UG, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PUNCTURE-RESISTING TIRE COMPOSITION AND ITS COATING METHOD		
(57) Abstract		
<p>This invention relates to a puncture-resisting tire composition comprising a thermoplastic elastomer, styrene-based block copolymer, as an active ingredient, unlike the conventional solvent-based rubber or emulsifier-based rubber containing some volatile substances. The viscous elasticity layer, so formed in such a manner to coat the puncture-resisting tire composition in a tire by a hot melting process at a very high temperatures, has excellent combination of advantages in that (1) since the viscous elasticity layer comprising a 100 % solid substance in the absence of organic solvent or water does not contain any volatile substance unlike the conventional solvent-based rubber or emulsifier-based rubber, it can shorten a prolonged period of time for evaporation of solvent used, (2) there is no risks of building fire or air contamination associated with the application of organic solvent, (3) the viscous elasticity layer can maintain a strong tackiness, even if large amounts of silicon mold release agent, anti-additive and anti-blocking agent are applied in a tire during its actual manufacture, (4) the viscous elasticity layer having the thickness of 1 ~ 5mm even at a short time of 10 ~ 20 seconds may be immediately applicable without any curing time, and (5) the viscous elasticity layer with a strong adhesiveness can exert an excellent puncture-resisting effect unlike the conventional solvent-or-water-evaporation method, since it is dissolved at a very high temperature and incorporated into the inside of tire thanks to more potent adhesiveness by several times.</p>		

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PUNCTURE-RESISTING TIRE COMPOSITION AND ITS COATING METHOD

Technical Field

This invention relates to a puncture-resisting tire composition and its coating
5 method and more particularly, to the puncture-resisting tire composition suitable for
application in a tubeless tire, and its hot-melting coating method for a tire.

Background Art

Generally, tires are divided into a tubeless tire and a tube-housed tire and recently,
10 a majority of vehicles have been equipped with a tubeless tire except for some freight cars
or omnibuses.

In case where nails are embedded in the tubeless tire, it is unlikely that its internal
pressure becomes lessen within a short time of period. Nonetheless, the tubeless tire will
face the same puncture problems as in the tube tire, under the following circumstances
15 where (1) with the gradually decreased air in the tubeless tire, a driver is operating his car
whose tire air is completely decreased, (2) some nails struck in the tubeless tire are slipped
during a high-speed, or (3) any vehicles are driving on the place where some gimlet-like
materials with pointed tips are embedded. If this happens, a fatal accident may be
unavoidable, or a driver has to repair the damaged tire for his re-driving.

20 A variety of methods, which may be classified into the following three types, have
been disclosed so as to avoid the risks associated with such tire puncture hitherto:

The first type has disclosed a method of letting a driver be known that a tire
puncture is responsible for gradual decrease of air since the driver using the tubeless tire,
can not immediately recognize the puncture (Korean laid-open Nos. 97-033989/97-
25 020487);

The second type is that even if there is a flat tire, a driver can continuously move

his vehicle to an appropriate place with additional means available (U.S. Patent No. 499893, Korean laid-open No. 92-000517, U.S. Patent No. 415468, and Korean laid-open No. 91-014246); and,

the third type is to fundamentally prevent a flat tire in such a manner that the
5 puncture-resisting composition is sealed to a tire.

Among these methods, the third type is further explained.

The conventional methods have disclosed the puncture-resisting tire composition as follows:

A method in which the inside wall of tire's crown is coated with a coal tar pitch or
10 a mixture of both petroleum pitch and polyisobutylene (Japanese publication No. 31-9489);

A method in which the inside wall of tire's crown is coated with a viscous rubber and then an air-flowing scrap of cloth such as a ring-shaped texture is combined into the rubber (Japanese publication No. 35-17402);

A method in which a hive structure of tire is compactly coated with a viscous
15 material containing a mixture of partially cross-linked polybutene, process oil and butyl rubber to form a sealing layer (Japanese publication No. 34-1095); and,

A method of using a sealant consisting of an ethylene-propylene rubber, polybutene and a filler (Japanese publication No. 50-39458).

However, these methods or some sealant for prevention of the flat tire have
20 recognized some disadvantages in that (1) the fluidity of puncture-resisting materials may occur at the cooling-flowing conditions or at a very high temperature, (2) the centrifugal force generated from the tire during a high speed driving has centered a sealant onto the central site of crown in a tire, (3) excess use of solvent is involved in human's safety problems and harmful environment in worksite, and (4) the sealing power of related
25 materials is not desirable for their actual application.

To overcome the aforementioned drawbacks, the Korean publication No. 82-652

has disclosed a solvent-type sealant composition, wherein one solution comprising a butyl rubber dissolved in a solvent, which is mixed with the other solution derived from polybutene, styrene-butadiene rubber and cross-linking agent, is sprayed to a tire rubber for curing, thus forming a sealing layer.

5 Since at least more than one solvent is employed in such sealant, however, the evaporation of solvent contained in a highly viscous polymer should require more prolonged time of period, even though a sealing material is coated at the thickness of 1mm. Therefore, the above patent has proposed that a sealant can be applied to a tire at the thickness of 1 ~ 3mm but its actual application appears to be difficult and unproductive,
10 despite the possibility that any sample manufacture may be available.

 Actually, a tire is manufactured in such a manner that a silicon-based mold release agent is coated in its inside, followed by the addition of large amounts of an anti-additive and anti-blocking agent. However, if the conventional sealant using a solvent or water as diluent is applied to the tire, a proper adhesiveness in a tire cannot be achieved, or a tire
15 may be cracked owing to poor adhesiveness, even if adhered. To comply with this matter, the coated surface of mold release agent needs to be completely eliminated, along with more prolonged time of period and enormous expenditures, thus being uneconomical as a consequence.

 In addition, the use of solvent-type paints using organic solvent may lead to severe
20 building fire or air contamination.

 With these problems that the conventional methods have encountered, the conventional sealant have yet to be commercialized for many years due to their poor adaptability and application in the industrial field.

25 **Disclosure of Invention**

 Therefore, an object of this invention is to provide a puncture-resisting tire

composition which has excellent combination of properties in that (1) the adhesiveness of an sealant is further enhanced in preventing a puncture of tire, (2) the flow of the composition into a crown site of tire can be prevented during a high-speed driving, and (3) any safety problem and harmful environment associated with excess use of solvent at
5 worksite can be also prevented.

Another object of this invention is to provide a puncture-resisting composition which can fundamentally improve a poor productivity due to more extended workability in line with the evaporation of solvent during sealing process.

Further object of this invention is to provide a puncture-resisting composition as a
10 100% solid form which can easily applied on a coating material such as a mold release agent present in the inside of tire during manufacture.

Further object of this invention is to provide a puncture-resisting composition containing no volatile substance which can prevent tire's damage caused by the remaining volatile substance and internal fluidity, together with a coating method to dissolve it in a
15 very high temperature.

Brief Description of the Drawings

FIG. 1 is a sectional view showing that a puncture-resisting composition is sealed onto a tire,

20 FIG. 2 is a schematic view showing the puncture-resisting principle of tire coated with the puncture-resisting composition.

Best Mode for Carrying out the Invention

To achieve the above objectives, the puncture-resisting tire composition of this
25 invention is characterized by a composition comprising a thermoplastic elastomer, which is styrene-based block copolymer, as an active ingredient, unlike the conventional solvent-

based rubber or emulsifier-based rubber containing some volatile substance, and its viscous elasticity layer is applied onto the inside of tire via a hot-melting process at a very high temperature.

According to this invention, the puncture-resisting tire composition comprises 100
5 weight parts of a styrene-based thermoplastic elastomer, 110 ~ 190 weight parts of an adhesive agent, 80 ~ 140 weight parts of a liquid plasticizer and 2 ~ 20 weight parts of an additive.

This invention is explained in more detail as set forth hereunder.

Each component comprising the puncture-resisting tire composition is explained
10 in more detail as follows:

(1) First composition: Styrene-based thermoplastic elastomer

The detailed examples of such compound include a styrene-butadiene-styrene block copolymer (hereinafter referred to as "SBS"), a styrene-isoprene-styrene block copolymer (hereinafter referred to as "SIS") and a styrene-ethylene-butylene-styrene block copolymer
15 (hereinafter referred to as "SEBS"). Even though these thermoplastic rubbers do not need to be cured, their strength has nearly same properties as some curing rubbers, while maintaining their elasticity up to -80 °C with better ozone resistance and chemical proofing.

(2) Second composition: Adhesive agent

The adhesive agent is a resin intended to provide the styrene-based thermoplastic
20 resin with a tackiness, and its detailed examples include a petroleum resin, a rosin, a rosin ester, a coumaron-indene resin, an acrylic resin with a high molecular weight, a ketone resin, a saturated aliphatic hydrocarbon-based resin and paraffin wax. The common adhesive agent as a solid form, which is mixed with a styrene-based resin, demonstrates a very high tackiness.

25 (3) Third composition: Liquid plasticizer

Examples of the liquid plasticizer include a process oil, polybutene and other

mineral oil. These materials serves to lower the viscosity, increase the elongation and facilitate the corresponding process.

(4) Fourth composition: Additive

Examples of the commonly used additives in the puncture-resisting tire composition
5 include an anti-oxidant, a wetting agent or a defoaming agent. These additives serve to prevent the discoloration of a final product and changes in physical property owing to oxidation at a very high temperature during heating and melting process.

When a tackifier is intended for manufacture based on the above chemical composition, a variety of desired products can be produced by changing the mixing ratio
10 of each component which may affect various properties such as tensile strength, elongation, tackiness, adhesiveness and melting point.

It is the most preferred that the puncture-resisting tire composition comprises 100 weight parts of the first composition, 110 ~ 190 weight parts of the second composition, 80 ~ 140 weight parts of the third composition and 2 ~ 20 weight parts of the fourth
15 composition.

If the content of the second composition is less than 110 weight parts in proportion to 100 weight parts of styrene-based thermoplastic elastomer, a tackiness becomes reduced but in case of exceeding 190 weight parts, there is a weak sealing layer and insufficient elasticity.

20 Further, if the content of the third composition is less than 80 weight parts in proportion to 100 weight parts of styrene-based thermoplastic elastomer, there is a reduced elongation and increased hardness; in case of exceeding 140 weight parts, the elongation is extremely high but strength and hardness becomes reduced.

To achieve the objectives of this invention, it is preferred that a sealant should be
25 extended until the whole body of a nail, so infiltrated, is fully covered; when a nail is slipped, a sealant is simultaneously flowed to occupy the corresponding gap. It is revealed

that the puncture-resisting tire composition of this invention can maintain the sealing state, even when the whole body of a nail, so infiltrated, is not fully covered.

To this end, the puncture-resisting tire composition of this invention having a larger tackiness and elongation is more advantageous but a higher elongation may lead to a poor tensile strength and excessive tackiness. Notwithstanding this, such problems may be
5 experimentally overcome in a simple manner.

Meantime, the puncture-resisting tire composition of this invention has a solid form fundamentally; in other words, the above composition is not applied to a tire in such a manner to be dissolved in water or solvent, being evaporated. Thus, the coating method of
10 sealing solution onto a tire is totally different from the common sealing solution.

The process designed to apply the puncture-resisting tire composition of this invention to a tire is performed in such a manner that a sealing solution, so prepared, is flowed into the inside of tire in a melting state (about 200 ~ 250 °C), without special treatment or sprayed under a high pressure for its easy sealing in the inside of tire. Then,
15 when a sealant with a strong adhesiveness is compactly attached to a tire, proper adhesion can be achieved irrespective of any mold release agent used for the manufacturing process of tire, thus obtaining more several-fold adhesiveness than the conventional method.

The thickness of a sealing layer in the puncture-resisting composition, so applied and formed in a tire, may vary depending on the work temperature and objective but it is
20 preferred that in consideration of its adhesiveness, the thickness of a sealing layer is in the range of 1 ~ 5mm, more preferably in the range of 2 ~ 3mm.

If a sealing layer is an extremely thick, the centrifugal force generated in the tire during a high speed driving has led a sealing composition to the central site of crown in a tire and may affect the weight of tire.

25 Meantime, FIG. 1 is a sectional view showing that the puncture-resisting composition is attached to a tire. FIG. 2 is a puncture-resisting principle of tire.

The puncture-resisting composition of this invention is explained based on the following principle in a subsequent manner:

When a nail is embedded in a tire, its whole body or the neighboring area is covered with a sealant as represented in FIG 2 (a), even when pierced. As represented in FIG 2 (b),
5 when the nail is beginning to slip, the sealant of this invention is simultaneously being flowed down. As represented in FIG. 2 (c), the nail is slipped in the middle of tire, the sealant is simultaneously accompanied by the nail. Finally, as represented in FIG. 2 (d), the sealant is simultaneously pressed out of tire together with the nail and then all spaces of the nail are occupied by the sealant. Thus, after the nail was completely removed from a tire,
10 the hole generated by the nail is completely re-occupied by the elasticity of rubber independently.

Based on such principle, the puncture-resisting composition of this invention can maintain its own sealing property for a long time of period, since it can completely reoccupy the gap, when a nail is removed.

15 This invention is explained by the following Examples in more detail as set forth hereunder but is not confined to these Examples.

Example 1

The puncture-resisting tire composition was prepared in such a manner that a mixture of 40 weight parts of rosin, 35 weight parts of rosin ester, 100 weight parts of
20 aliphatic hydrocarbon-based polymer (PICOFALE#95, Hercules Co.), 80 weight parts of process oil, and 3 weight parts of additive (IRGANOX#1076, Ciba-Geigy Co.) was added to 100 weight parts of SBS, followed by its stirring and homogenization process.

Example 2

The puncture-resisting tire composition was prepared in such a manner that a
25 mixture of 90 weight parts of petroleum resin, 90 weight parts of rosin ester, 90 weight parts of process oil, and 5 weight parts of additive (IRGANOX#1076, Ciba-Geigy Co.) was

added to 100 weight parts of SEBS, followed by its stirring and homogenization process.

The inside of a tire, which was treated with a mold release using silicon oil and talc, was sealed with the puncture-resisting composition, so prepared from Examples 1 and 2, at the thickness of about 2mm by a hot-melting flowing process.

- 5 The sealed tire installed to a rim was under air infusion and then the following tests was performed at the pressure of 34 psi (pound per inch square):

To investigate the air leakage of tire, 20 nails (length: 8cm, thickness: 4mm) were embedded at the side portion of tire including the tread site and placed in water. However, no air leakage in a tire was observed. When an automobile with the sealed treated tire was
10 driven at the speed of 80km/mph, 100km/mph and 120km/mph for 20 minutes each at Express Highway, there was no air leakage in the tire.

After driving, the test after removing all of the 20 nails showed that there was no air leakage. Further, the air leakage tests at a refrigerator (-30 °C) and an oven (80 °C) after 2 hours, no air leakage in a tire was observed.

- 15 After a 5-day test, there was no air leakage in a tire.

After removing all nails from the tire, the results of actual driving tests at Express Highway and in downtown road showed that there was no air leakage in the tire, except for some abrasion in tire only.

Example 3

- 20 The puncture-resisting tire composition was prepared in such a manner that a mixture of 70 weight parts of rosin, 110 weight parts of aliphatic hydrocarbon-based polymer (PICOTAC#95, Hercules Co.), 80 weight parts of polybutene, and 2 weight parts of anti-oxidant (IRGANOX#1076, Ciba-Geigy Co.) was added to 100 weight parts of SBS, followed by its stirring and homogenization process.

- 25 A tire was sealed with each of puncture-resisting tire composition, so prepared, at the thickness of about 2.0mm in the same manner as Example 1 and 2.

The following tests were performed under the same pressure as Example 1. To investigate the air leakage of tire, 40 nails (length: 8cm, thickness: 4mm) were embedded at the crown and shoulder portions of tire and placed in water. However, no air leakage in a tire was observed.

- 5 Further, the tire was placed at an oven (80 °C) for 2 hours and when 10 nails was removed, it was revealed that the sealing state of tire was perfect, since some sealed solution was flowed out of the removed hole of nails. Also, no air leakage in a tire was observed.

- 10 An automobile equipped with the above tire was driven at Express Highway at the speed of 110km/mph and in downtown road for 1 week, respectively. After driving, the remaining 30 nails were removed to investigate the air leakage of tire but no change was observed. After a 1-week parking, there was no air leakage of tire. Further, when the tread portion of tire was pierced with a gimlet (diameter: 10mm), no air leakage in a tire was observed.

15 **Example 4**

- The puncture-resisting tire composition was prepared in such a manner that a mixture of 85 weight parts of rosin ester and rosin, 100 weight parts of aliphatic hydrocarbon-based polymer (HICORES c-1100, Kolon Co.), 62 weight parts of process oil and polybutene and 3 weight parts of additive (IRGANOX#1076, Ciba-Geigy Co.) was
20 added to 110 weight parts of SEBS.

Example 5

- The puncture-resisting tire composition was prepared in such a manner that a mixture of 150 weight parts of rosin, 25 weight parts of acrylic resin in solid form, 80 weight parts of process oil and 2 weight parts of anti-oxidant (IRGANOX#1076, Ciba-
25 Geigy Co.) was added to 100 weight parts of SEBS.

 A tire was sealed with each of puncture-resisting tire composition, so prepared from

Examples 4 and 5, at the thickness of 1.5 ~ 2.0mm in the same manner as Example 1 and 2, followed by housing the tire to a rim. The following tests were performed at the same pressure as Example 1.

To investigate the air leakage of tire, an automobile equipped with the puncture-resisting tire was driven at the speed of 50km/mph through a board (thickness: 2cm, width: 20cm, length: 2m) embedded with each nail (length: 7mm, thickness: 4mm) at each distance interval of 20cm, which was turned inside out. However, no air leakage in a tire was observed.

After a 1-week test, there was no air leakage in a tire. Further, the air leakage tests at a refrigerator (-30 °C) and an oven (80 °C) after 2 hours, no air leakage in a tire was observed.

As mentioned in the above, an sealant of this invention, so prepared by using a thermoplastic elastomer, which is a styrene-based or its similar block copolymer, as an active ingredient instead of a solvent-based rubber, including an adhesive agent, liquid plasticizer and other additive, has the following advantages in that (1) unlike the conventional sealant, the sealant of this invention has no cooling and/or fluidity problem, (2) the sealant of this invention has significantly shortened the prolonged time of solvent's evaporation, (3) prior to coating the sealant of this invention to a tire, there is no need to separately remove a mold release agent, anti-additive and anti-blocking agent in a tire, (4) an excellent puncture-resisting effects of the composition can be demonstrated immediately after its sealing on tire, and (5) the sealant of this invention can be easily attached to a newly generated tire by a direct high-pressure spray and flowing method, thus proving to be very practical.

25 Industrial Application

In addition, the puncture-resisting tire composition of this invention may be

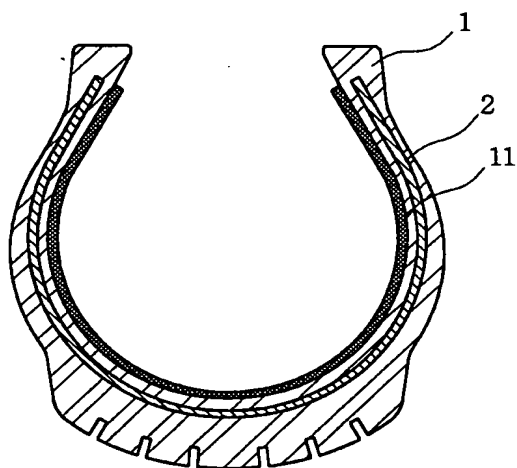
applicable to all tires of vehicles such as tubeless tires, tube tires, motorcycle tires, bicycle tires, and industrial tire. In this context, it is needless to say that these applications are in the scope of the claims as specified hereunder.

What is claimed is:

1. A puncture-resisting tire composition comprising 100 weight parts of a styrene-based thermoplastic elastomer, 110 ~ 190 weight parts of an adhesive agent, 80 ~ 140 weight parts of a liquid plasticizer and 2 ~ 20 weight parts of an additive.
5
2. The puncture-resisting tire composition according to claim 1, wherein one or more of said styrene-based thermoplastic elastomer is/are selected from the group consisting of styrene-butadiene-styrene block copolymer, styrene-isoprene-styrene block copolymer, and styrene-ethylene-butylene-styrene block copolymer.
10
3. The puncture-resisting tire composition according to claim 1, wherein one or more of said adhesive agents is/are selected from the group consisting of petroleum resin, rosin, rosin ester, coumaron-indene resin, acrylic resin with a high molecular weight, ketone resin, saturated aliphatic hydrocarbon-based resin, and paraffin wax.
15
4. The puncture-resisting tire composition according to claim 1, wherein one or more of said liquid plasticizer is/are selected from the group consisting of a process oil, polybutene and mineral oil.
- 20 5. The puncture-resisting tire composition according to claim 1, wherein one or more of said additives is/are selected from the group consisting of an anti-oxidant, a wetting agent and a defoaming agent.
- 25 6. A process for coating the puncture-resisting tire composition, wherein the puncture-resisting tire composition according to claim 1 is applied, in a melting state, to the inside of tire via high-pressure spray or flowing method.

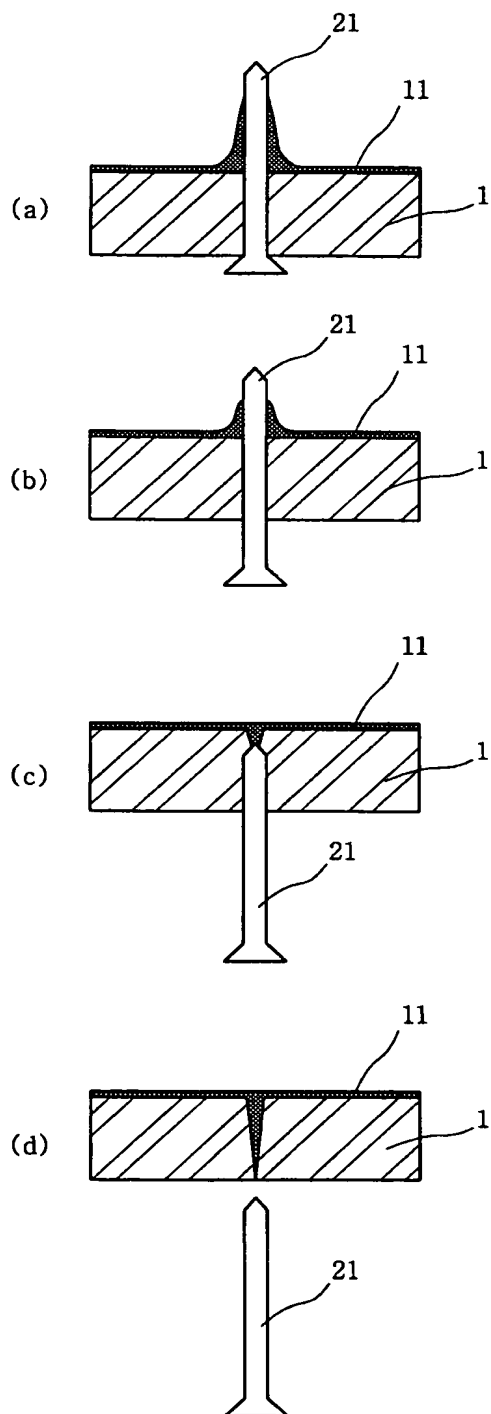
7. A process for coating the puncture-resisting tire composition according to claim 6, wherein the coating process of said puncture-resisting tire composition is made in such a manner that the thickness of the coating layer is in the range of 1 ~ 5mm.

FIG. 1



2/2

FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR 99/00261

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁶: C 08 L 25/04; B 60 C 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC⁶: C 08 L, B 60 C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Online database: WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 302 400 A1 (THE UNIROYAL GOODRICH TIRE COMPANY), 02 August 1989 (02.08.89), page 5, line 25 - page 6, line 42; examples; claims.	1-7
A	US 4 109 695 A (MIYAZATO), 29 August 1978 (29.08.78), fig.2,3; examples; claims.	1-7
A	Derwent Abstracts AN 79-27112B [14], 01 March 1979 (01.03.79), JP 54-027 105 (BRIDGESTONE CORP.), abstract.	1-7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

27 August 1999 (27.08.99)

Date of mailing of the international search report

03 September 1999 (03.09.99)

Name and mailing address of the ISA/AT

Austrian Patent Office
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/KR 99/00261

In Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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